

Article

Influence of Lanthanum Doping on the Photocatalytic and Antibacterial Capacities of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Fe}_2\text{O}_4$ Nanoparticles

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Abstract: The increase in environmental pollution, especially water pollution, has intensified the requirement for new strategies for the treatment of water sources. Furthermore, the improved properties of nano-ferrites permit their usage in wastewater treatment. In this regard, novel $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ nanoparticles (NPs), where $0.00 \leq x \leq 0.08$, were synthesized to test their photocatalytic, antibacterial and antibiofilm activities. The structural and optical properties of the prepared NPs were investigated by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), UV-Vis spectroscopy and photoluminescence (PL) analysis. As La content increases, the bandgap energy increases, whereas the particle size decreases. The photocatalytic activity of the prepared NPs is evaluated by the degradation of methylene blue (MB) dye under sunlight irradiation. Superior activity is exhibited by $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs. The influence of catalyst dosage, pH, temperature and addition of graphene (Gr) on the photodegradation reaction was studied. Increasing the pH and temperature improved the rate of the photodegradation reaction. The antibacterial and antibiofilm activities of the NPs were assessed against *Escherichia coli*, *Leclercia adecarboxylata*, *Staphylococcus aureus* and *Enterococcus faecium*. $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Fe}_2\text{O}_4$ NPs inhibited bacterial growth. They had bacteriostatic activity on all isolates, with a greater effect on Gram-positive bacteria. All tested nano-ferrites had significant antibiofilm activities against some biofilms.

Keywords: $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$; photocatalytic activity; methylene blue photodegradation; antibacterial activity; antibiofilm activity; wastewater treatment



Citation: Rabaa, M.; Mezher, M.; Aridi, A.; Naoufal, D.; Khalil, M.I.; Awad, R.; Abdeen, W. Influence of Lanthanum Doping on the Photocatalytic and Antibacterial Capacities of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Fe}_2\text{O}_4$ Nanoparticles. *Catalysts* **2023**, *13*, 693. <https://doi.org/10.3390/catal13040693>

Academic Editors: Yuanhua Sang and Zupeng Chen

Received: 8 March 2023

Revised: 27 March 2023

Accepted: 30 March 2023

Published: 2 April 2023



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1. Introduction

The most fundamental component for the survival of living things is water. A healthier life is facilitated by the usage of clean and safe water. However, large amounts of dye-containing effluents are discharged untreated into the water, which, in turn, causes water pollution [1]. Dyes, characterized by their cheap production and stability, are widely used in textiles, paper, plastics, leather, printing, cosmetics and coatings. Dye-containing water affects human and animal health and is visible in water even at very low concentrations (<1 ppm) [2]. Furthermore, microbiological water pollution is recognized as one of the

major problems across the world [3]. Consequently, removing pollutants such as bacteria and dyes from wastewater is highly desirable.

Magnetic NPs are characterized by their unique properties that are not observed in bulk materials. These characteristics can be attributed to the finite size effects, high surface-to-volume ratio and distinct crystal structures. Numerous physical, chemical and biological techniques can be employed to synthesize these NPs. However, choosing the preparation technique depends on the targeted morphology, size, properties and application of the NPs [4]. The co-precipitation method is recognized for its simplicity, affordability and wide size distribution. Furthermore, it gives rise to NPs that can be functionalized in several applications, including catalysis, gas sensing and antibacterial applications [5,6]. Owing to their size, structures and unique optical and magnetic properties, NPs have been used in a variety of fields, including the electrical and electronic industries and the biomedicine field [7]. Various types and structures have been investigated, including the hexagonal and spinel ferrites. Studies on ferrites are fast-moving, owing to their exponentially growing usage in magnetic biosensors, magnetic shielding, information storage, magnetic recording devices, electronic devices, mobile communication, pollution control, medical devices, transformers and catalysis [8].

Concerning the role of nano-ferrites as a pollutant control, they stand out among the most efficient advanced materials in terms of their potential to remove pollutants [9]. This is due to the economic profile and efficiency of nano-ferrites, which permit their usage in the removal of various pollutants such as pesticides, dyes, medicines and hazardous chemicals. In addition, the improvement of the properties of ferrites can be done by modifying the synthesis parameters and the doping or formation of nano-composites [10]. The doping of rare earth metals, such as Samarium (Sm) and Lanthanum (La), improves the surface-to-volume ratio and enhances the optical, electrical and magnetic properties of host materials [11]. For example, doping CoFe_2O_4 with La improved the magnetic properties, reduced the bandgap energy and increased the surface area [12]. The improved properties permit their usage in environmental applications. Furthermore, La-doped BiFeO_3 NPs exhibited superior catalytic performance in the photodegradation of Rhodamine B dye compared to that of pure BiFeO_3 NPs [13]. As for the antibacterial activity, magnetic NPs were shown to exhibit a significant antibacterial activity, depending on their shape, size and density of oxygen vacancies [14]. In addition, rare earth metals were shown to exert unique antibacterial advantages, especially against *Escherichia coli* and *Staphylococcus aureus*. They act by penetrating the bacterial cells and changing the cytoplasmic composition, thus leading to the destruction of the bacterial cells [15]. Regarding water treatment, some studies reported that La-doped NPs can remove pollutants and microbes, such as *Klebsiella pneumoniae* and other pathogens, during the treatment process. This activity is inversely proportional to the size, as the antibacterial activity can be enhanced by smaller-sized NPs [16].

Among several spinel ferrites, MgFe_2O_4 , NiFe_2O_4 and CoFe_2O_4 NPs have attracted the attention of scientists and are useful due to their unique characteristics. It is known that MgFe_2O_4 is a soft magnetic semiconducting material with a normal spinel structure [17]. NiFe_2O_4 , having an inverse spinel structure, is a soft magnetic semiconducting material [18]. Whereas CoFe_2O_4 , characterized by its inverse spinel structure, is classified as a semi-hard material [19]. Thus, it is interesting to investigate the properties of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Fe}_2\text{O}_4$ NPs. As mentioned before, doping ferrites with rare earth metals improves their properties. In this work, La-doped $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ spinel ferrites where $0.00 \leq x \leq 0.08$ were synthesized using the co-precipitation technique. In addition, the prepared NPs were characterized by XRD, TEM, UV and PL techniques. Finally, La-doped $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs were used to disinfect water from methylene blue (MB) dye and bacteria.

2. Results and Discussion

2.1. Characterization of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs

Figure 1 displays the refined and raw XRD patterns of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs, where $0.00 \leq x \leq 0.08$. The XRD pattern of pure $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Fe}_2\text{O}_4$ NPs ($x = 0.00$) reveals peaks that are located at 30.1° , 35.6° , 36.7° , 43.2° , 53.5° , 57.1° and 62.3° , corresponding to (220), (311), (222), (400), (422), (511) and (440) crystal planes, respectively. The peaks are matched with the standard JCPDS card no. 36-0398 and indexed to the cubic spinel phase with space group $\text{Fd}\bar{3}\text{m}$ [20]. Furthermore, the presence of hematite (Fe_2O_3) as a secondary phase is revealed from the presence of an extra peak located at $2\theta = 32.9^\circ$. Though, upon doping the NPs with La, the intensity of the peak—referring to the impurity phase—disappears. The absence of any extra peak in the XRD patterns of La-doped NPs ensures the purity of the prepared samples. It is worth mentioning that the values of the lattice parameter (a) of all doped NPs, listed in Table 1, are greater than that of pure NPs. This is mainly attributed to the substitution of Fe^{3+} with La^{3+} , knowing that the ionic radius of La^{3+} (1.06 Å) is greater than that of Fe^{3+} (0.65 Å). Similar behavior was reported in a previous study where the lattice parameter (a) increased upon doping $\text{Ni}_{0.3}\text{Zn}_{0.5}\text{Co}_{0.2}\text{La}_x\text{Fe}_{1.98-x}\text{O}_4$ ferrite with La [21].

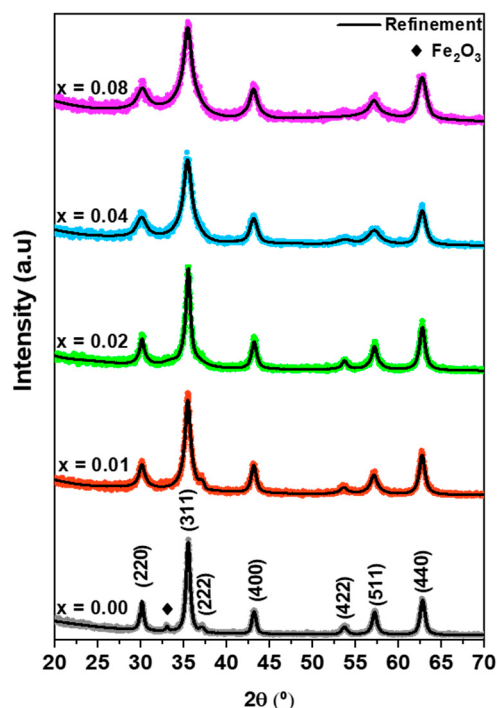


Figure 1. Raw and refined XRD patterns of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

Table 1. The values of lattice parameter (a), particle size (D_{TEM}) and bandgap energy (E_g) of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

x	a (Å)	D_{TEM} (nm)	E_g (eV)
0.00	8.351(3)	28.72	2.92
0.01	8.366(5)	25.98	3.18
0.02	8.354(4)	25.09	3.19
0.04	8.363(1)	22.79	3.22
0.08	8.372(5)	20.20	3.25

The particle size distribution and microstructure of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs, where $0.00 \leq x \leq 0.08$, were examined by TEM analysis and represented in Figure 2. The results indicate the synthesis of nano-sized particles with rounded-cube morphology.

Similar morphology of CoFe_2O_4 , MgFe_2O_4 and NiFe_2O_4 is reported in previously published studies [22–24]. Moreover, as La content increases from 0.00 up to 0.08, the particle size decreases from 28.72 to 20.20 nm, as shown in Figure 2 and Table 1. The reduction in the particle size, upon doping $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Fe}_2\text{O}_4$ with La, is attributed to the settling of the La^{3+} ions at grain boundaries, which inhibits the growth of the grains. Similar behavior is reported in a previous study, where the particle size of $\text{Ni}_{0.3}\text{Zn}_{0.5}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ NPs was reduced upon doping with Gd^{3+} and La^{3+} ions [25]. Furthermore, the aggregation of the synthesized NPs might be attributed to the magnetic dipole interaction among them [12].

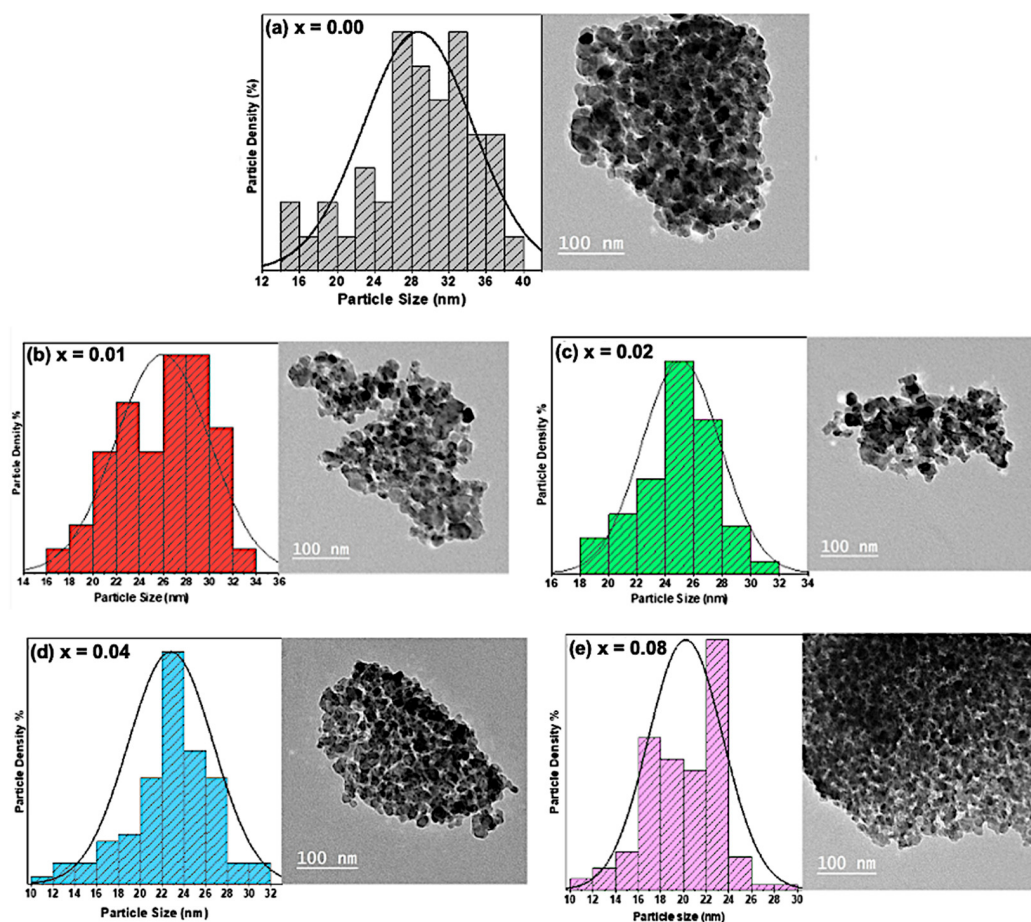


Figure 2. Particle size distribution and TEM images of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.04$ and (e) $x = 0.08$.

The UV-Vis absorption spectra of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$, in the range of 300–700 nm, are represented in Figure 3. A noticeable peak appears at 335 nm in the absorption spectra of all the prepared NPs. Comparable UV spectra of ferrite NPs, mainly $\text{Zn}_{0.5}\text{Mg}_{0.5-x}\text{Li}_{2x}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$, are stated in previous studies [26,27]. The prepared NPs with various La content exhibited stronger UV absorption, as revealed by the increased absorption intensity. Similar behavior also was reported by Lemziouka et al. [28] upon increasing La content in $\text{ZnFe}_{2-x}\text{La}_x\text{O}_4$ NPs. To better understand the change in optical properties caused by the doping of NPs with La, the optical bandgap energy was calculated. The bandgap energy (E_g) was estimated from Tauc's plot, which is represented in the following equation:

$$(\alpha h\nu)^2 = B (h\nu - E_g), \quad (1)$$

where α is the absorption coefficient, $h\nu$ represents the incident photon energy and B denotes the transition probability constant. Thus, the bandgap energy (E_g) was estimated

by plotting $(\alpha h\nu)^2$ vs. $h\nu$, as displayed in Figure 4 and Table 1. As La content increases from $x = 0.00$ to 0.08, E_g increases from 2.92 to 3.25 eV. The increase in E_g may result from intrinsic absorption and optical scattering at grain boundaries [29]. In addition, the increase in the bandgap energy accompanied by the decrease in the particle size upon increasing the La content is owed to the quantum size effect [29,30].

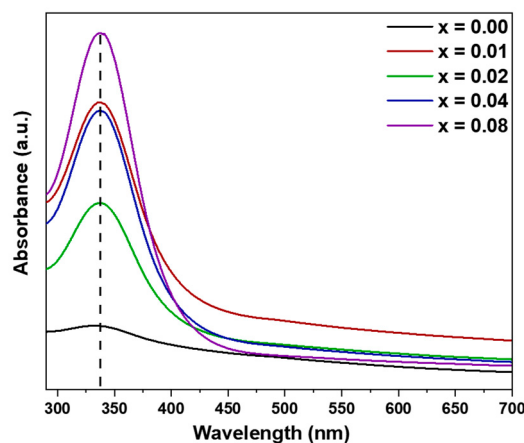


Figure 3. UV-Vis spectra of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

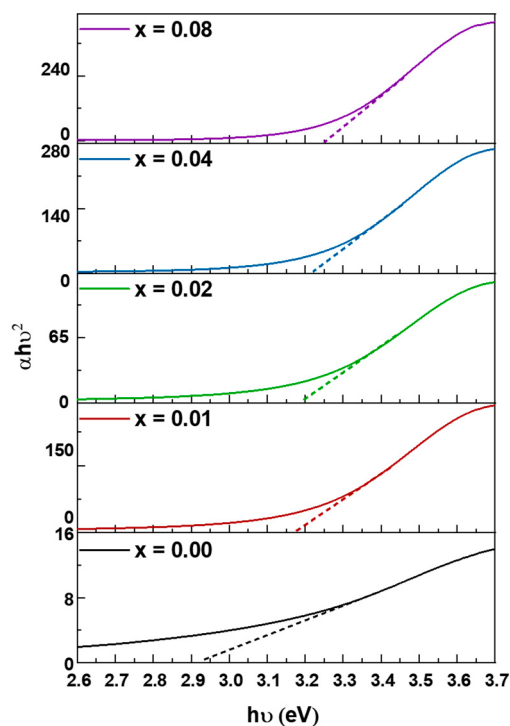


Figure 4. Tauc's plot of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

It is obvious that when a semiconductor gets exposed to light that has a wavelength equal to or higher than its bandgap energy, it absorbs the light. This causes the excitation of electrons from the valence band to the conduction band, creating a positive hole in the valence band. Thus, an electron-hole pair is generated. The electron-hole pair can either recombine or move from the semiconductor's surface to the solvent. It is worth mentioning that the photocatalytic activity of the semiconductor is subsequently decreased as a result of the recombination of electron-hole pairs. Furthermore, the recombination rate of the electron-hole pair can be measured by the intensity of PL emission. Thus, the PL investigation was carried out at room temperature by applying an excitation wavelength $\lambda_{\text{ext}} = 330$ nm, and the results are displayed in Figure 5a,b. Numerous peaks are

detected in UV and visible ranges. Due to the presence of oxygen vacancies and intrinsic imperfections, peaks appear in the visible region. However, the peak located in the UV region at 3.7 eV is attributed to the recombination of the electron-hole pair. Upon doping $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Fe}_2\text{O}_4$ with La, the intensity of this peak is reduced. Thus, the recombination rate becomes slower. In addition, NPs with La content of 0.01 and 0.04 exhibited the slowest recombination rate of the electron-hole pair.

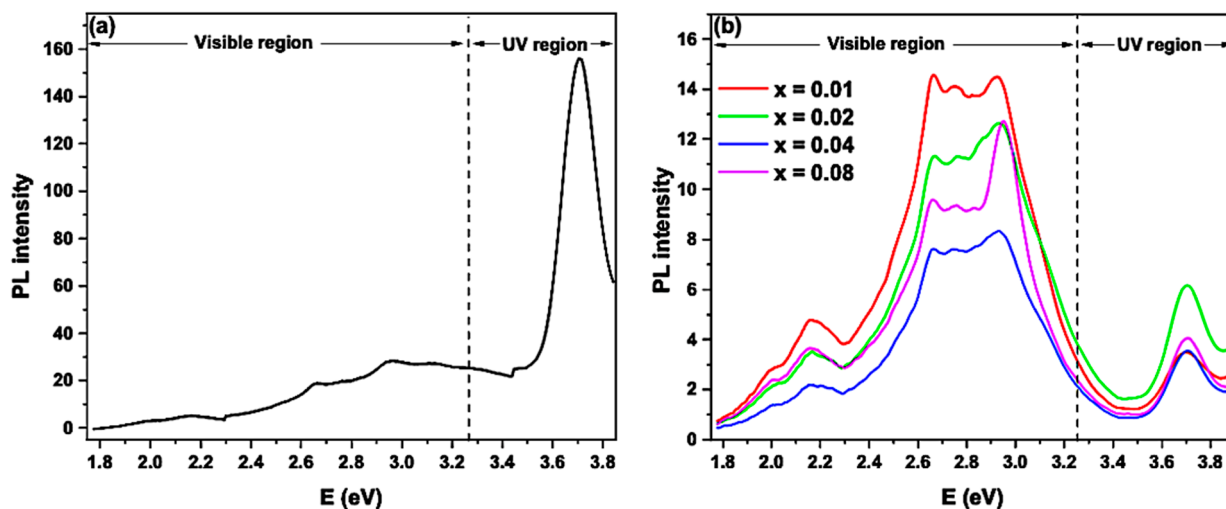


Figure 5. PL spectra of (a) pure $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{Fe}_2\text{O}_4$ ($x = 0.00$) and (b) $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.01 \leq x \leq 0.08$.

2.2. Photocatalytic Activity of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs

The photocatalytic properties of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0 \leq x \leq 0.08$ were evaluated by the degradation of MB dye under direct sunlight. The linear plot of $\ln C_0/C_t$ vs. time (Figure 6 and Table 2) revealed, from high R^2 values, the first-order kinetics. So, the rate law for the MB photodegradation reaction is given as follows [31]:

$$\ln (C_0/C_t) = kt, \quad (2)$$

where C_0 is the concentration of MB at time $t = 0$ and C_t is the concentration at any time t and k is the degradation rate constant. As listed in Table 2, the rate constant k increases from 29×10^{-4} to $37 \times 10^{-4} \text{ min}^{-1}$ as x increases from 0 to 0.01; whereas, as x increases to reach 0.08, rate constant k decreases to reach $17 \times 10^{-4} \text{ min}^{-1}$. Among the prepared doped samples, an improved photocatalytic activity is exhibited in the presence of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ with $x = 0.01$.

Table 2. Rate constant (k) and coefficient of determination (R^2) for the photodegradation of MB dye in the presence of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

x	$k \times 10^{-4} (\text{min}^{-1})$	R^2
0.00	29	0.997
0.01	37	0.972
0.02	5	0.944
0.04	16	0.965
0.08	17	0.953

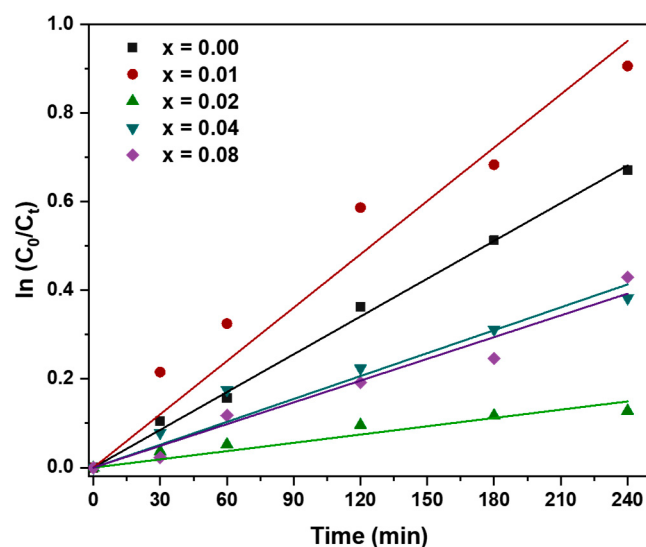


Figure 6. $\ln(C_0/C_t)$ vs. sunlight irradiation time for the photodegradation of MB dye in the presence of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

$\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs revealed the lowest PL peak intensity of the peak located at 3.7 eV, showing the slowest recombination rate of the photogenerated electron-hole pair. Among the doped samples, $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs exhibited the highest PL peak intensity of the peaks located in the visible region, revealing the presence of increased oxygen vacancies. The presence of oxygen vacancies plays an important role in enhancing the photocatalytic performance of NPs [32,33]. Thus, the photocatalytic performance of NPs is in good accordance with the PL results.

Whenever the mixture of MB and NPs is placed under sunlight, light absorption by NPs will occur. Consequently, electron-hole pairs are generated. Since $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs revealed the slowest recombination rate of the photogenerated electron-hole pair, the electron-hole pair will migrate to the NPs' surface. It is worth mentioning that the uncombined electron-hole pair interacts with the O_2 and H_2O and produces reactive species, such as hydroxyl radicals ($\text{OH}\cdot$), superoxide radicals ($\text{O}_2^{\cdot-}$) and H_2O_2 . Finally, the produced reactive species are responsible for the degradation of MB dye through a direct oxidation process [34,35].

2.2.1. Effect of Photocatalyst Dosage

After demonstrating that the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ exhibited an enhanced photocatalytic activity, the effect of photocatalyst dosage was studied by performing the photodegradation reaction of MB in the presence of different amounts of photocatalyst (0.04, 0.06, 0.08 and 0.1 g). As shown in Figure 7, as the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ amount increases from 0.04 to 0.06 g, the rate of the reaction increases from 29×10^{-4} to $35 \times 10^{-4} \text{ min}^{-1}$. This is because the active sites of the catalyst increase with increasing the amount of photocatalyst [36]. However, with a further increase in the catalyst amount to 0.1 g, the reaction rate decreases to reach $15 \times 10^{-4} \text{ min}^{-1}$. The presence of an excess amount of catalyst (more than 0.06 g) scatters the sunlight and thus blocks its penetration into the reaction. Therefore, the rate of the reaction starts decreasing. Furthermore, additional amounts of NPs lead to particle agglomeration, which, in turn, reduces photon absorption that takes place on the surface [37]. Thus, 0.06 g is the recommended dosage of the catalyst.

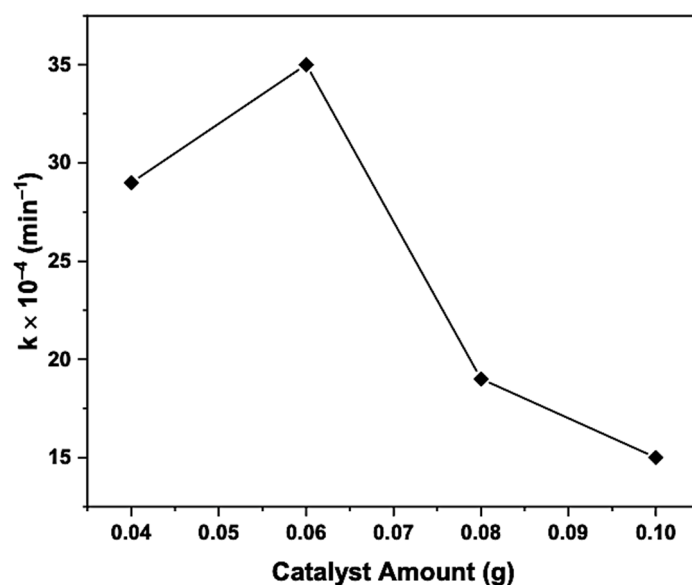


Figure 7. The variation of rate constant (k) for the photodegradation of MB dye in the presence of different amounts of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs.

2.2.2. Effect of pH

One of the key variables in the photocatalytic property of substances is the solution's pH. This is explained by the fact that the pH affects the adsorption behavior of the pollutants as well as the chemical characteristics of the photocatalyst. So, at pH values ranging from 2.47 to 10.73 (acidic, neutral and basic pH values), the effect of pH on the photocatalytic degradation of MB in the presence of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs was investigated. As shown in Table 3, the rate constant increases from 7×10^{-4} to $517 \times 10^{-4} \text{ min}^{-1}$ when the pH rises from 2.47 to 10.73. Thus, the rate of the photodegradation reaction of MB is 73.8 and 14.7 times higher in the basic medium (pH = 10.73) compared to that studied in the acidic (pH = 2.47) and neutral (pH = 6.27) medium, respectively. So, the solution's ideal pH is basic. As reported in previous studies, the point of zero charge (PZC) of MgFe_2O_4 , NiFe_2O_4 and CoFe_2O_4 NPs was 8.4, 6.4 and 7.2, respectively [38–40]. If the pH is less than the PZC, the surface of NPs will be positively charged; when the pH is greater than the PZC, the negative form of the NPs is more likely to exist [37]. Being a cationic dye, MB is positively charged in the solution. Consequently, the MB dye is attracted to the negatively charged catalyst surface due to opposite charges. Thus, increasing the pH of the solution improves the photocatalytic degradation of MB. Identical results were reported in a previous study, where the pH = 12 solution was the optimal medium for the photodegradation of MB by biosynthesized ZnFe_2O_4 NPs [41].

Table 3. Rate constant (k) for the photodegradation of MB dye in the presence of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs in different media.

pH	$k \times 10^{-4} \text{ (min}^{-1}\text{)}$
2.47	7
4.05	23
6.27	35
9.75	39
10.73	517

2.2.3. Effect of Temperature

To investigate the effect of temperature, the photodegradation reaction was carried out at 313, 323, 328 and 333 K. The obtained results are displayed in Figure 8. As the reaction temperature increases from 313 to 333 K, the rate constant increases from 11×10^{-4}

to $58 \times 10^{-4} \text{ min}^{-1}$. Thus, increasing the reaction temperature boosts the rate of the photodegradation reaction of MB. This is attributed to the generation of electron-hole pairs that can be produced more quickly at higher temperatures, causing improved photocatalytic activity. In other words, as reaction temperature increases, more electrons are transferred from the valence band to the conduction band. Consequently, excessive electron-hole pairs are generated. This, in turn, increases the production of reactive radicals that are responsible for the degradation of MB dye. A similar trend has been detected for the degradation of MB in the presence of the $\text{Fe}_2\text{O}_3/\text{graphene}/\text{CuO}$ photocatalyst [42].

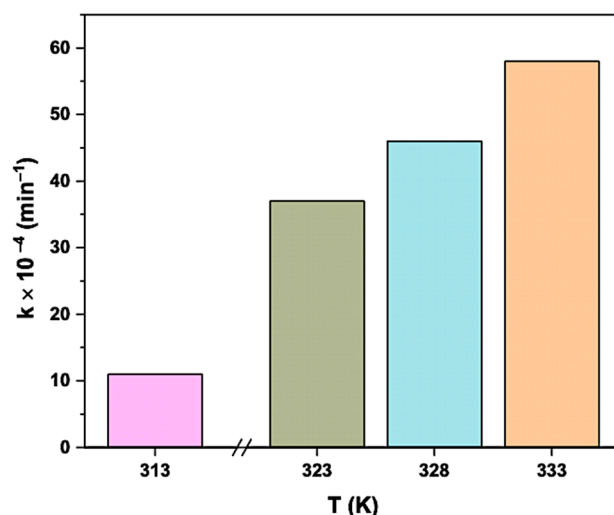


Figure 8. Variation of the rate constant (k) for the photodegradation reaction of MB dye performed at different temperatures in the presence of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs.

2.2.4. Thermodynamic Parameters

The thermodynamic parameters can be estimated by performing the photodegradation reaction of the MB dye at various temperatures. Figure 9 and Table 4 display the results. The activation energy (E_a) and the frequency factor (A) were calculated from the slope and intercept of the logarithmic form of the following Arrhenius equation [43]:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (3)$$

where k is the rate constant, R is the universal gas constant, which is equal to $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and T is the temperature. E_a and A were calculated from the slope and intercept of the linear plot of $\ln k$ vs. $1/T$. Additionally, the slope and intercept of the plot of $\ln(k/T)$ vs $(1/T)$ were used to estimate the enthalpy (ΔH) and entropy change (ΔS), as shown in the following equation [43]:

$$\ln \frac{k}{T} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

Table 4. Thermodynamic parameters of the photodegradation reaction of MB dye.

T (K)	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)	A (min^{-1})	ΔH ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	ΔG ($\text{kJ}\cdot\text{mol}^{-1}$)
313	73.02	19.02×10^8	70.34	121.3	32.38
323					31.16
328					30.56
333					29.95

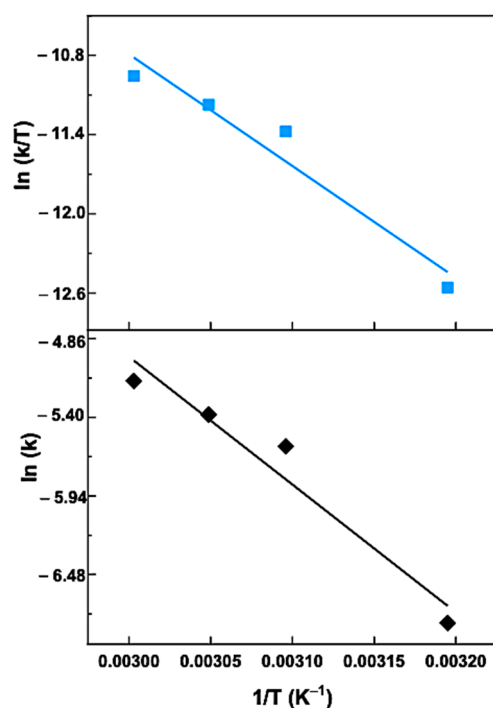


Figure 9. Plots of $\ln(k)$ and $\ln(k/T)$ vs. $(1/T)$.

Additionally, the following relationship was used to determine the Gibbs free energy change (ΔG):

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

2.2.5. Influence of Graphene Addition

Since electron-hole recombination severely restricts photocatalytic activity, several techniques are employed to boost the charge carrier separation effectiveness and, consequently, the photocatalytic performance of the photocatalyst. The combination of graphene (Gr) with the photocatalyst constitutes a novel approach in this situation [44]. The impact on photocatalysts of mixing various weight percentages of Gr with 0.06 g $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ was examined. The obtained results are shown in Figure 10a. Furthermore, the degradation %, displayed in Figure 10b, was calculated using the following equation:

$$\text{Degradation \%} = \frac{C_0 - C_t}{C_0} \times 100 \quad (6)$$

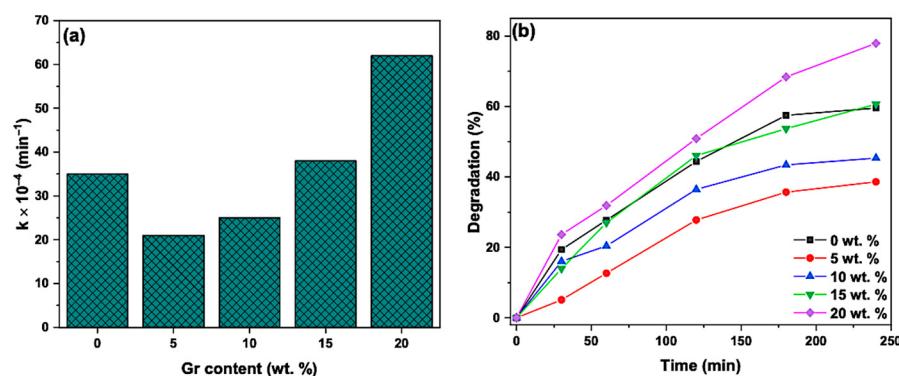


Figure 10. (a) The rate constant (k) and (b) degradation % of the photodegradation of MB dye in the presence of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs combined with different wt.% of Gr.

The rate of the reaction decreases to $25 \times 10^{-4} \text{ min}^{-1}$ with the addition of Gr up to 10 wt %. However, with a further increase in the Gr content of up to 20 wt.%, the rate of the degradation reaction increases. The photodegradation of the MB is greatly improved when 20 wt.% of Gr is combined with $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs. Moreover, 77.9% of MB dye was degraded after sunlight exposure time up to 240 min in the presence of 20 wt.% Gr/ $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ nanocomposites (NCs). This might be ascribed to the effective charge transfer encouraged by Gr addition, which enhances the separation of the photogenerated electron-hole pair [45]. Therefore, the combination of NPs with Gr significantly enhanced the photocatalytic activity of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs in the MB degradation, and 20 wt.% of Gr is the ideal Gr content. To confirm that the formation of heterojunction between Gr and NPs is the reason behind the improvement of catalytic activity, the photodegradation of MB was evaluated in the presence of pure Gr. As shown in Figure 11, the degradation reaction of MB proceeds 1.24 and 1.77 times faster in the presence of 20 wt.% Gr/ $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NCs compared to that in the presence of pure Gr and $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs, respectively.

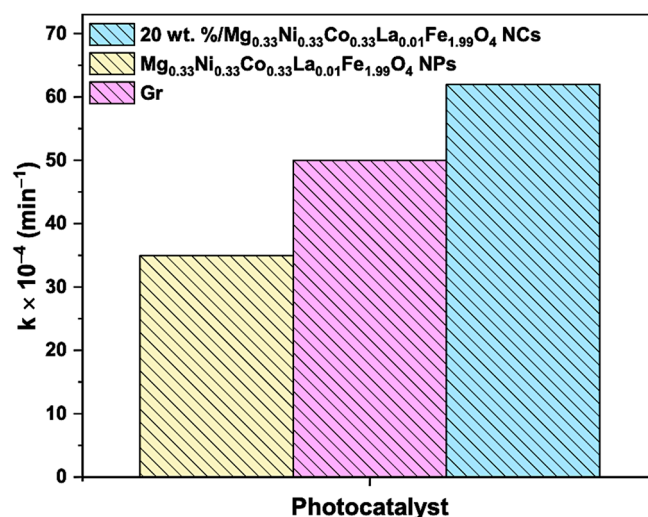


Figure 11. Rate constant (k) for the photodegradation of MB dye in the presence of Gr, $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NPs and 20 wt.% Gr/ $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NCs.

2.2.6. Optimal Experimental Conditions

The reaction's rate was studied by applying the optimal experimental conditions. To do this, the pH of the MB dye solution was adjusted to 10.73 before being combined with 0.06 g of 20 wt.% Gr/ $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.01}\text{Fe}_{1.99}\text{O}_4$ NCs. According to Figure 12, when exposure time increases, the intensity of the MB peak—which is positioned around 675 nm—decreases. Furthermore, after applying the ideal conditions, it is important to note that the rate constant of the degradation reaction of MB is boosted to reach 0.0619 min^{-1} and 96.8% is degraded after 60 min. The results obtained from this study were compared with published reports for the degradation of MB under sunlight radiation in the presence of various nano-ferrites, as listed in Table 5. Superior photocatalytic performance was exhibited by NPs prepared in this study in the degradation of MB dye.

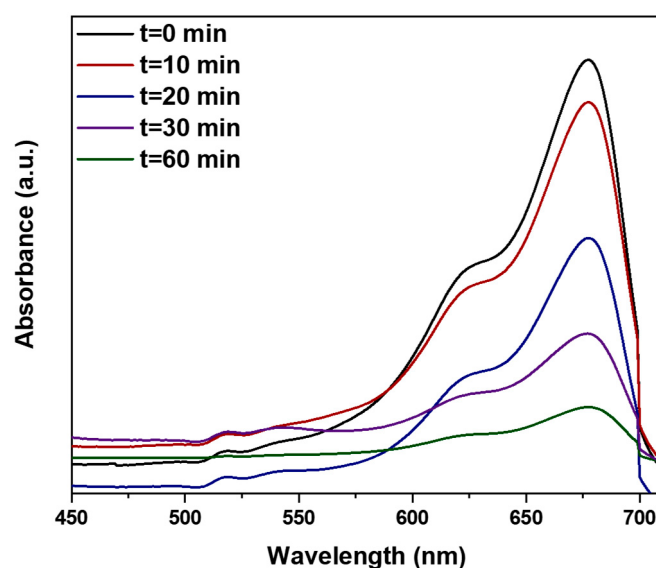


Figure 12. UV-Vis spectra of MB dye solution extracted at different times from the reaction.

Table 5. Comparison with published reports for the degradation of MB under sunlight radiation in the presence of various nano-ferrites.

Photocatalyst	Amount (mg)	k (min ^{−1})	Ref.
Ni _{0.5} Cu _{0.5} Fe ₂ O ₄		0.032	
Ni _{0.3} Co _{0.2} Cu _{0.5} Fe ₂ O ₄	50	0.037	[46]
Co _{0.5} Cu _{0.5} Fe ₂ O ₄		0.045	
5% Y-BiFeO ₃	100	0.0163	[47]
Mg _{0.5} Zn _{0.5} Fe ₂ O ₄	-	0.00236	[48]
NiFe ₂ O ₄		0.00408	
Ag-doped NiFe ₂ O ₄ @ rGO	20	0.00859	[49]
Cu doped MgFe ₂ O ₄		0.00316	
MgFe ₂ O ₄ @ rGO	20	0.00994	[50]
Mg _{0.33} Ni _{0.33} Co _{0.33} La _{0.01} Fe _{1.99} O ₄ NPs		0.0035	
20 wt.%Gr/Mg _{0.33} Ni _{0.33} Co _{0.33} La _{0.01} Fe _{1.99} O ₄ NCs	60	0.0619	Current study

2.3. The Antibacterial Activity of the Mg_{0.33}Ni_{0.33}Co_{0.33}La_xFe_{2-x}O₄ NPs

The increase in the discard of wastes in the environment leads to an increase in pollution rates, especially water pollution. To decrease this pollution, researchers suggested the incorporation of NPs, especially nano-ferrites, in this field. This is due to their significant effects on decreasing the heavy metals and inhibiting the growth of microorganisms [51]. In this regard, this study reported the effect of Mg_{0.33}Ni_{0.33}Co_{0.33}La_xFe_{2-x}O₄ NPs where $0.00 \leq x \leq 0.08$ on four bacteria (*Escherichia coli*, *Leclercia adedecarboxylata*, *Staphylococcus aureus* and *Enterococcus faecium*) isolated from wastewater.

2.3.1. MICs and MBCs of the Mg_{0.33}Ni_{0.33}Co_{0.33}La_xFe_{2-x}O₄ NPs where $0.00 \leq x \leq 0.08$

Bacteria were incubated with increasing concentrations (0.375–3 mg/mL) of each of the NPs. At the used concentration range of NPs, the only bacteriostatic effect that was detected was that of the Mg_{0.33}Ni_{0.33}Co_{0.33}La_{0.00}Fe₂O₄ NPs. It had the best inhibitory activity against *Leclercia adedecarboxylata* and *Enterococcus faecium*. In contrast, *Escherichia coli* was the most resistant. The MIC and MBC assays didn't detect any inhibitory activity for the Mg_{0.33}Ni_{0.33}Co_{0.33}La_xFe_{2-x}O₄ NPs where $0.01 \leq x \leq 0.08$ against any of the tested bacterial isolates (*Staphylococcus aureus*, *Enterococcus faecium*, *Escherichia coli* and *Leclercia adedecarboxylata*). The results are shown in Table 6 and Figures A1 and A4. All results were significant, with *p*-values < 0.05. Previous studies showed that La-doped NPs exert good antibacterial activity. For example, Anitha et al. reported that La-doped nano-oxides had

an effectual action against microorganisms due to the high density of oxygen vacancies, which leads to an increase in the reactive oxygen species (ROS) production [51]. In addition, spinel ferrites were shown to inhibit bacterial growth, especially methicillin-resistant *Staphylococcus aureus* (MRSA). This is caused by damaging the cell walls and membranes of the bacterial cells [52]. However, the observed results in this work could be attributed to the difference in the composition of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs, in which the inhibitory action depends mainly on the structure of the NP as well as the tested bacterium. The characterization profiles revealed an increase in the bandgap energy upon doping of the nano-ferrites. This bandgap energy decreases the antibacterial activity of the NPs, as reported by Ansari et al. [52], who worked on nano-spinel ferrites and showed a decrease in antibacterial activity, especially against *Staphylococcus aureus*. In addition, this weak inhibitory effect may be due to the decrease in the oxygen vacancies upon doping. This also affects the antibacterial activity of the NPs, due to the decrease in the production of reactive oxygen species (ROS). This is consistent with previous studies that showed that antibacterial activity is enhanced by the production of ROS [53,54].

Table 6. The MICs and MBCs of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

x	MICs and MBCs (mg/mL)	Gram-Negative Bacteria		Gram-Positive Bacteria	
		<i>Escherichia coli</i>	<i>Leclercia adecarboxylata</i>	<i>Staphylococcus aureus</i>	<i>Enterococcus faecium</i>
0.00	MIC	3	0.375	1.5	0.375
	MBC	>3	>3	>3	>3
	MBC/MIC	>1	>8	>2	>8
0.01	MIC	>3	>3	>3	>3
	MBC	>3	>3	>3	>3
	MBC/MIC	>1	>1	>1	>1
0.02	MIC	>3	>3	>3	>3
	MBC	>3	>3	>3	>3
	MBC/MIC	>1	>1	>1	>1
0.04	MIC	>3	>3	>3	>3
	MBC	>3	>3	>3	>3
	MBC/MIC	>1	>1	>1	>1
0.08	MIC	>3	>3	>3	>3
	MBC	>3	>3	>3	>3
	MBC/MIC	>1	>1	>1	>1

MIC: minimum inhibitory concentration, MBC: minimum bactericidal concentration.

2.3.2. Agar Well Diffusion Results of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$

The agar well diffusion results of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$ were in accordance with the results of the MIC and MBC assays. The $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NP where $x = 0.00$ had significant antibacterial activity, especially against *Leclercia adecarboxylata* and *Enterococcus faecium*. None of the doped NPs showed any zone of inhibition (ZOI) against any of the tested bacterial isolates. The results are shown in Table 7 and Figure A5. All results were significant, with p -values < 0.05 , and are shown in Table A1. The observed results may be explained by the TEM observations, which showed that the tested NPs are spherical in shape. Previous studies showed that spherical nanoparticles are less effective than sharp-edged NPs [55–57]. Moreover, the agglomeration of the NPs—revealed by the XRD results—also may affect the antibacterial activity. Agglomeration increases the size of NPs, which decreases their capability to penetrate bacterial cells. Li et al. reported that agglomeration should be treated in the NPs before their use in water treatment because it decreases the effectivity of the NPs [56,58,59].

Table 7. Agar well diffusion of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_{0.00}\text{Fe}_{2-x}\text{O}_4$ NPs.

Nanoparticles		Bacterial Isolates			
		Gram-Negative Bacteria <i>Escherichia coli</i>	<i>Leclercia ade-carboxylata</i>	Gram-Positive Bacteria <i>Staphylococcus aureus</i>	<i>Enterococcus faecium</i>
Sample	Concentration (mg/mL)	ZOI $\pm$ SEM (mm)			
x = 0.00	0.375	4.6 $\pm$ 0.16	7.3 $\pm$ 0.13	5.6 $\pm$ 0.23	7.3 $\pm$ 0.08
	0.75	5.6 $\pm$ 0.42	8.6 $\pm$ 0.32	6.6 $\pm$ 0.25	7.3 $\pm$ 0.13
	1.5	6.6 $\pm$ 0.02	9.6 $\pm$ 0.24	10.3 $\pm$ 0.36	8.6 $\pm$ 0.24
	3	10.6 $\pm$ 0.38	10.6 $\pm$ 0.29	11.3 $\pm$ 0.30	9.6 $\pm$ 0.24

None of the doped nanoparticles showed any zone of inhibition (ZOI) against any of the tested bacterial isolates. SEM: standard error of the mean.

2.3.3. Antibiofilm Activity of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$

Surprisingly, the La-doped NPs had a good inhibitory effect against some of the bacterial biofilms, especially against *Enterococcus faecium*. The other biofilms were more resistant, especially *Escherichia coli*. Similarly, good eradication activity was recorded, especially against *Leclercia adedecarboxylata* and *Enterococcus faecium*. On the other hand, *Escherichia coli* and *Staphylococcus aureus* were more resistant. Both the biofilm inhibition and eradication were similar after 24 and 48 h of incubation. The results of biofilm inhibition are shown in Table 8 and Figure A2, and those of biofilm eradication are shown in Table 9 and Figure A3. All results were significant, with a *p*-value < 0.05. This surprising result, knowing that the doped NPs had no MIC and MBC, could be explained by the ability of the small-sized NPs to penetrate the cells of the biofilm, leading to their dispersion and preventing their attachment. In addition, these results are similar to a previous study, which reported a significant anti-biofilm activity of nano-ferrites, especially against *Staphylococcus aureus* and *Enterococcus columbae* [60]. This action is attributed to the interaction of the NPs with the exopolysaccharides and the proteins exerted by the biofilms for attachment, thus preventing the formation of the biofilm [52,60]. In accordance with the use of the same concentrations of the nano-ferrites on the bacterial biofilms in the current study, morphological changes in the bacterial cells were observed, followed by complete lysis of the cells, thus destroying the pre-formed biofilms [61].

Table 8. Inhibition of the formation of bacterial biofilms by the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

Nanoparticles	Incubation Time (Hours)	Bacterial Isolates and Concentration of Inhibition (mg/mL)			
		Gram-Negative Bacteria <i>Escherichia coli</i>	<i>Leclercia ade-carboxylata</i>	Gram-Positive Bacteria <i>Staphylococcus aureus</i>	<i>Enterococcus faecium</i>
x = 0.00	24	-	-	0.375	-
	48	-	0.375	0.75	3
x = 0.01	24	-	3	0.75	-
	48	-	-	0.75	-
x = 0.02	24	-	-	0.75	1.5
	48	-	-	0.75	-
x = 0.04	24	-	1.5	0.75	0.75
	48	-	-	0.75	-
x = 0.08	24	-	3	1.5	0.75
	48	-	-	1.5	-

Table 9. Eradication of the pre-formed biofilms by the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

Nanoparticles	Incubation Time (Hours)	Bacterial Isolates and Concentration of Inhibition (mg/mL)			
		Gram-Negative Bacteria		Gram-Positive Bacteria	
		<i>Escherichia coli</i>	<i>Leclercia ade-carboxylata</i>	<i>Staphylococcus aureus</i>	<i>Enterococcus faecium</i>
x = 0.00	24	-	0.75	-	1.5
	48	-	0.75	0.75	3
x = 0.01	24	-	0.375	-	0.75
	48	-	1.5	3	1.5
x = 0.02	24	-	0.75	-	-
	48	-	3	-	0.375
x = 0.04	24	-	-	-	3
	48	-	3	3	0.75
x = 0.08	24	-	1.5	-	-
	48	-	-	3	-

3. Materials and Methods

3.1. Synthesis of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs Where $0.00 \leq x \leq 0.08$

The La-doped magnesium-nickel-cobalt ferrite NPs were prepared by the co-precipitation method. The required masses of magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), cobalt (II) chloride hydrate ($\text{CoCl}_2 \cdot \text{H}_2\text{O}$), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and lanthanum (III) chloride hexahydrate ($\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$) were dissolved in deionized water and stirred for 30 min. The mixture was titrated by careful addition of 3 M sodium hydroxide (NaOH) solution until the pH reached 12. Then, the obtained solution was heated at a temperature of 80 °C, with constant magnetic stirring for 2 h. After that, the solution was kept at room temperature for 10 min to cool down. This was followed by filtration and washing of the obtained precipitate with a solution of 75% deionized water and 25% ethanol until the pH dropped to 7. The obtained precipitates were then dried at 100 °C for 18 h and finally annealed at 550 °C for 4 h.

3.2. Characterization Techniques

XRD patterns were recorded in the range of $20^\circ \leq 2\theta \leq 80^\circ$ using $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.54056 \text{ \AA}$) by X ray diffractometer (D8 Advance, Bruker, Billerica, United states). The morphology and size of the prepared samples were evaluated by TEM using JEM-1400 Plus (JEOL, Tokyo, Japan). To perform the UV test, 0.01 g of each of the prepared NPs was dissolved in 50 mL of 1 M HCl solution. Afterward, the mixtures were sonicated for 5 min. Subsequently, the optical properties of the samples were estimated by ultraviolet-visible (UV-Vis) spectroscopic examinations that were performed at room temperature in the range of 300–700 nm using UV-Vis spectrophotometer (V-670, JASCO, Tokyo, Japan). The PL spectra were recorded at room temperature between 1.8 and 3.9 eV at an excitation wavelength of 330 nm via a fluorescence spectrometer (FP8300, JASCO, Tokyo, Japan).

3.3. Photocatalytic Activity of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs

The photocatalytic activity of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs, where $0.00 \leq x \leq 0.08$, was examined by mixing 0.06 g of each catalyst with 100 mL of 3 ppm methylene blue (MB) solution. The obtained solutions were then stirred for 30 min in the darkness to achieve the adsorption-desorption equilibrium. Then, the mixture was placed under direct sunlight between 11 am and 2 pm. The photodegradation reactions were performed in August. The effect of the catalyst dose, temperature, pH and graphene (Gr) addition was investigated. To study the effect of pH on the photodegradation reaction, a few drops of 0.5 M HCl and NaOH were added to adjust the pH of MB solution between 2 and 11. Furthermore, to prepare nanocomposites with 5, 10, 15 and 20 wt.% Gr, 0.003, 0.006, 0.009 and 0.012 g of Gr, respectively, were mixed with 0.06 g of the most efficient catalyst using 10 mL ethanol solution. Afterward, the mixture was sonicated for 20 min

and placed in the oven at 70 °C to remove the ethanol. 3 mL of the MB solution was taken at different time intervals and analyzed using a UV-Vis spectrophotometer (SPECORD 200, Analytik Jena, Thuringia, Germany).

3.4. Antibacterial Activity of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs

3.4.1. Bacterial Isolation and Identification

Bacteria were isolated from wastewater samples. 100 µL of the isolated bacteria were spread on agar plates containing different selective media. The plates were then incubated at 37 °C for 24 h. Then, the bacterial isolates were Gram stained for differentiating between Gram-positive and Gram-negative bacteria prior to VITEK (VITEK 2 Automated Systems, bioMérieux Inc., Massachusetts, United states) for further identification of the bacterial species [62].

3.4.2. Determination of the Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC) by the Microdilution Method

The MICs of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$ were determined by the micro-well dilution assay. The assay was done by dispensing 90 µL of nutrient broth (NB) into the wells of sterile 96-well microplates. Following that, 10 µL of previously prepared bacterial suspensions adjusted to 0.5 McFarland were added to the wells. Then, 100 µL of each NP of different concentrations (0.375–3 mg/mL) were added to the wells. The microplates were then incubated for 24 h at 37 °C. After incubation, the optical density (O.D.) was measured at 595 nm by an ELISA microtiter plate reader (SN 357-912359, Thermo Fisher Scientific, Shanghai, China). The MIC was recorded as the lowest concentration of the NPs that inhibited visible growth of the bacteria. Following the MIC recording, 10 µL of the solutions in the clear wells were spread on plates containing Muller Hinton agar (MHA) and incubated for 24 h at 37 °C for detecting the MBC [63]. All experiments were repeated at least three times.

3.4.3. Determination of the Zones of Inhibition (ZOI) by the Agar Well Diffusion Assay

The agar well diffusion assay was performed by evenly spreading 100 µL of the isolated bacterial suspensions (0.5 McFarland) over the surface of the MHA plates. The plates were then punched with a 6 mm cork-borer to create wells. Then, 100 µL of increasing concentrations of each NP (0.375–3 mg/mL) were added to the wells. The plates were then incubated for 24 h at 37 °C. After incubation, the diameter of the ZOI was measured, in which $\text{ZOI} > 7$ mm was considered effective [64,65]. All experiments were repeated at least three times.

3.4.4. Antibiofilm Activity of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs

• Inhibition of bacterial biofilm formation

The biofilm inhibition assay was done to determine the potential of $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$ to prevent the formation of biofilms. The assay was done by adding 100 µL of bacterial cultures into 96-well microtiter plates and incubating for 4 h at 37 °C to allow the attachment/formation of the biofilms. Then, 100 µL of increasing concentrations of each NP (0.375–3 mg/mL) were added to the wells. A culture medium without any inoculum was used as a negative control. The plates were incubated at 37 °C for 24 and 48 h. The biomass was quantified by the crystal violet (CV) staining technique. Briefly, following the incubation period, the plates were washed with sterile distilled water 5 times, then air-dried and oven-dried for 15 min at 60 °C. Then, 100 µL of 1% CV was added to the wells and incubated for 15 min at room temperature. To remove the unabsorbed stain, the plates were washed with sterile distilled water 5 times and the biofilms were observed in the form of purple rings. To de-stain the wells, 100 µL of 95% ethanol was then added. Finally, the O.D. was measured at 595 nm using an ELISA microplate reader (SN 357-912359, Thermo Fisher Scientific, Shanghai, China) [66]. All experiments were repeated at least three times.

The percentage of inhibition of the formation of the bacterial biofilms was determined using the following equation:

$$\% \text{ Inhibition} = \frac{O.D. (\text{negative control}) - O.D. (\text{treated})}{O.D. (\text{negative control})} \times 100 \quad (7)$$

- Eradication of pre-formed bacterial biofilms

The potential of the NPs to eradicate the pre-formed bacterial biofilms was tested by adding 100 μ L of the standard cultures of the bacterial isolates into 96-well microtiter plates and incubating for 30 h at 37 °C to form the biofilms. After incubation, 100 μ L of increasing concentrations of each NP (0.375–3 mg/mL) were added into the wells and the plates were incubated at 37 °C for 24 and 48 h. A culture medium without any inoculum was considered the negative control. The biomass of each biofilm was detected by CV staining, and the percentage of eradication of the pre-formed bacterial biofilms was determined as mentioned above in the inhibition of the formation of biofilms [66]. All experiments were repeated at least three times.

3.4.5. Statistical Analyses

The statistical tests were done using Excel software. The graphs were drawn using Origin software. The statistical significance was determined by *t*-Test.

4. Conclusions

Mg_{0.33}Ni_{0.33}Co_{0.33}La_xFe_{2-x}O₄ NPs where $0.00 \leq x \leq 0.08$ were successively synthesized by the co-precipitation method. As *x* increases from 0.00 to 0.08, *E_g* increases from 2.92 to 3.25 eV, whereas *D_{TEM}* decreases from 28.72 to 20.20 nm. Doping Mg_{0.33}Ni_{0.33}Co_{0.33}La_xFe_{2-x}O₄ NPs with La enhanced their photocatalytic performance. Among the prepared NPs, enhanced photocatalytic activity was exhibited by NPs where *x* = 0.01. This was attributed to the slow recombination rate of the electron-hole pair, as revealed by PL analysis. In addition, the optimal catalyst amount was 0.06 g. Furthermore, the incorporation of 20 wt.% of graphene (Gr) improved the photocatalytic activity of Mg_{0.33}Ni_{0.33}Co_{0.33}La_{0.01}Fe_{1.99}O₄ NPs. Among the tested NPs, the Mg_{0.33}Ni_{0.33}Co_{0.33}La_{0.00}Fe₂O₄ NPs had antibacterial activity. An antibiofilm action was observed for some of the doped NPs, especially those where *x* = 0.01, 0.02 and 0.04, mainly against biofilms of Gram-positive bacteria. Due to their high antibiofilm activity, the Mg_{0.33}Ni_{0.33}Co_{0.33}La_{0.00}Fe_{2-x}O₄ NPs are applicable in the biomedical field, especially against bacterial pathogens.

Author Contributions: Conceptualization, D.N., M.I.K., R.A. and W.A.; Data curation, M.R., M.M. and A.A.; Formal analysis, M.R., M.M., A.A. and M.I.K.; Investigation, M.R., M.M., A.A., D.N., M.I.K., R.A. and W.A.; Methodology, M.R., M.M., A.A., D.N., M.I.K. and R.A.; Resources, D.N., M.I.K., R.A. and W.A.; Software, M.M. and A.A.; Supervision, D.N., M.I.K., R.A. and W.A.; Validation, M.I.K. and R.A.; Writing—original draft, M.R., M.M. and A.A.; Writing—review & editing, M.R., M.M., A.A., D.N., M.I.K., R.A. and W.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

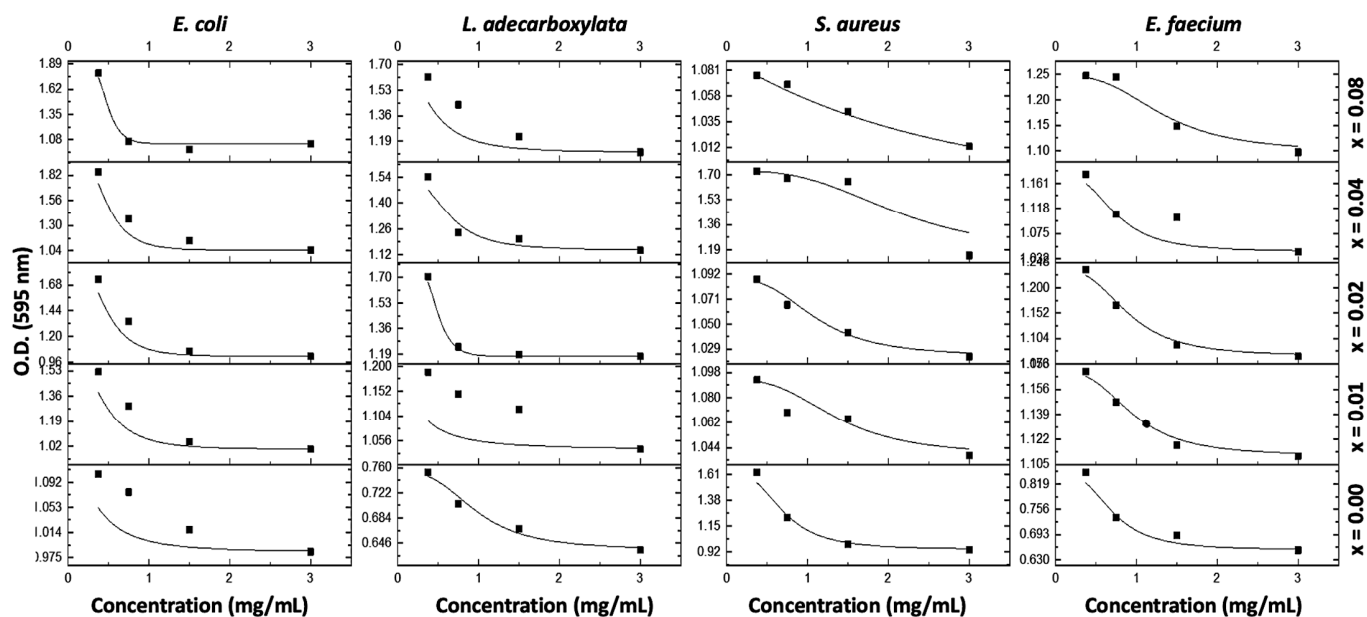
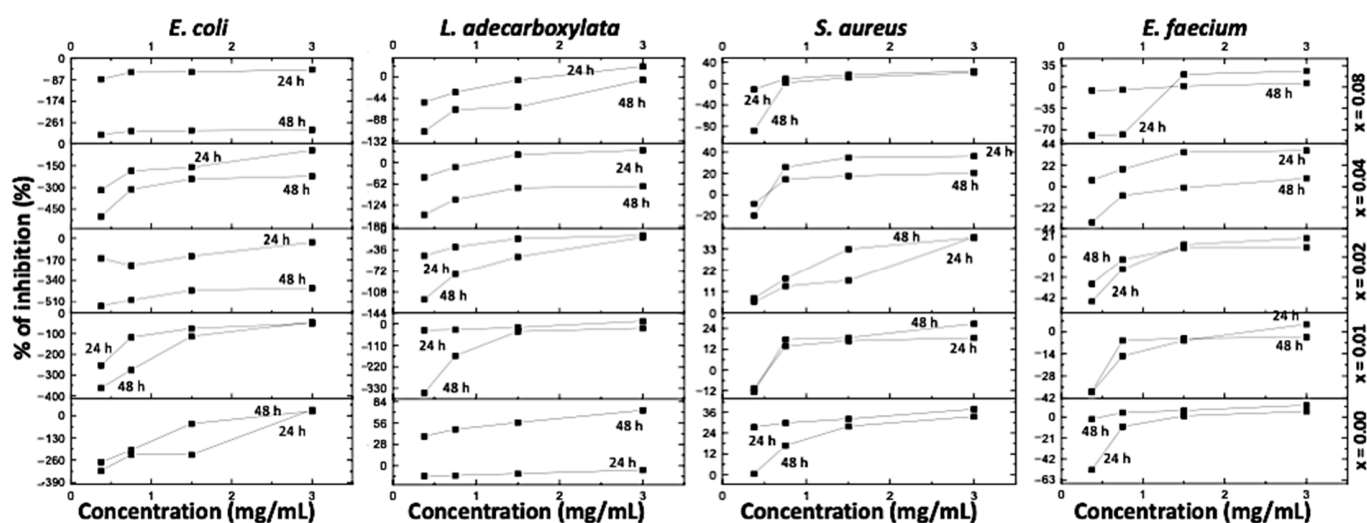
Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data supporting the reported results are available with the corresponding author and will be provided upon request.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Figure A1. MICs of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.Figure A2. Inhibition of the formation of bacterial biofilms by the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

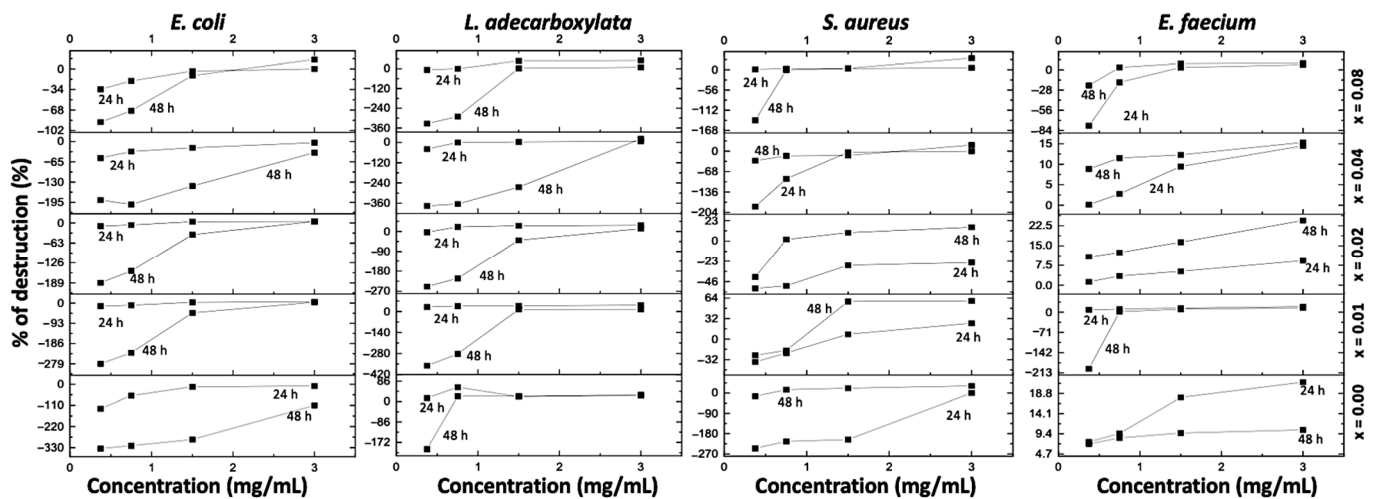


Figure A3. Eradication of the pre-formed bacterial biofilms by the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

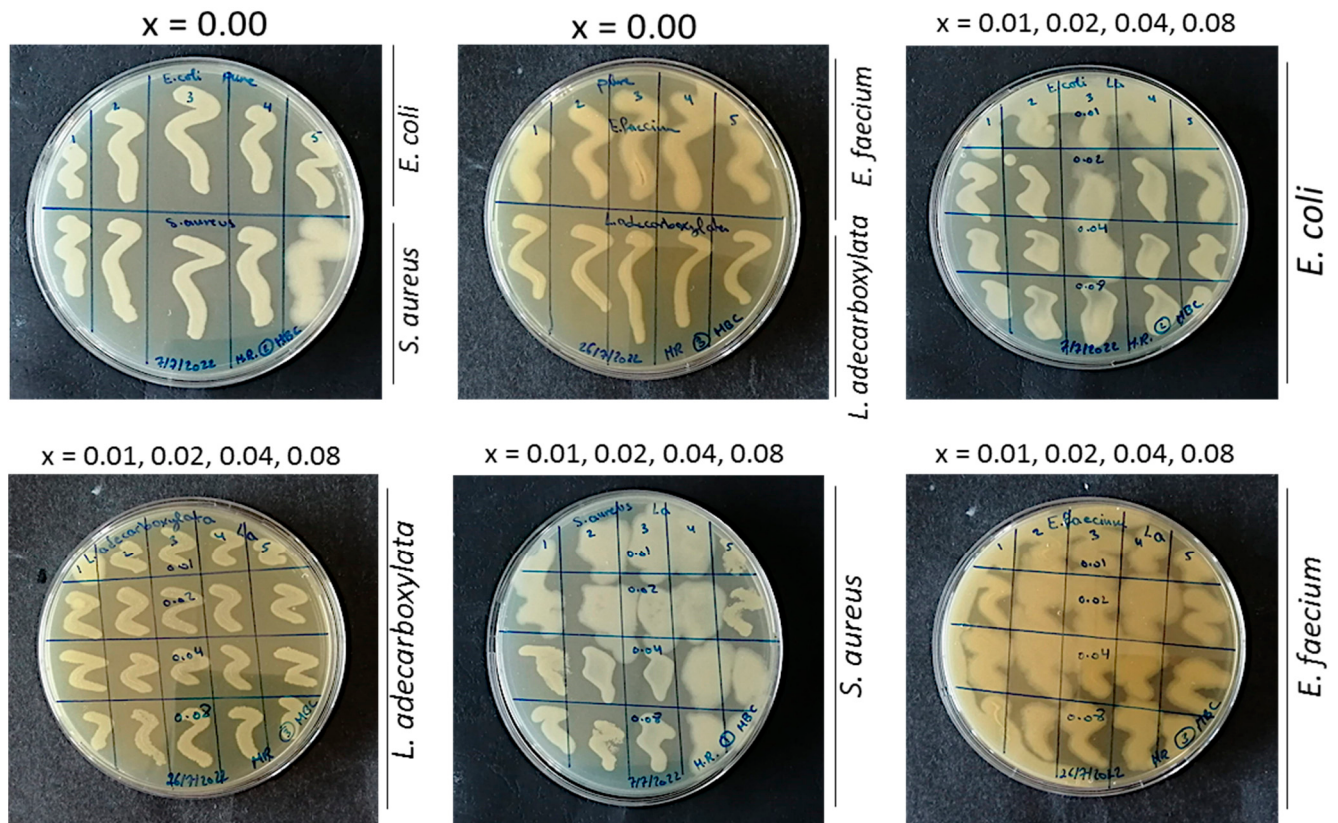


Figure A4. MBCs of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

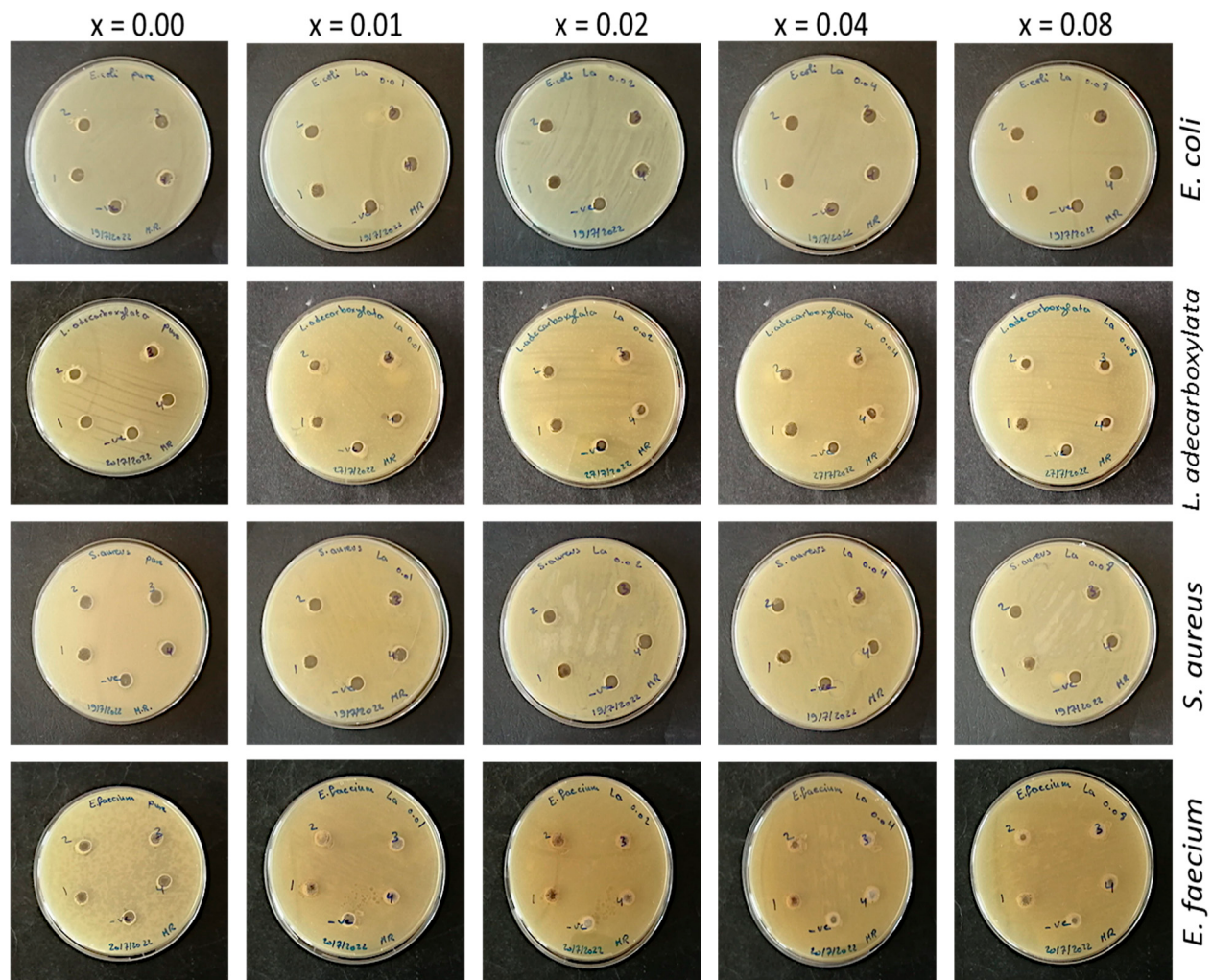


Figure A5. Agar well diffusion results of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

Table A1. p -values and significance levels of the agar well diffusion results of the $\text{Mg}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{La}_x\text{Fe}_{2-x}\text{O}_4$ NPs where $0.00 \leq x \leq 0.08$.

Nanoparticles		Bacterial Isolates							
		Gram-Negative Bacteria				Gram-Positive Bacteria			
		<i>Escherichia coli</i>	S	<i>L. eclerciaade-carboxylata</i>	S	<i>Staphylococcus aureus</i>	S	<i>Enterococcus faecium</i>	S
Sample	Concentration (mg/mL)	<i>p</i> -Values (vs. Water)							
x = 0.00	0.376	0.005	**	0.002	**	0.003	**	0.002	**
	0.75	0.003	**	0.001	***	0.002	**	0.002	**
	1.5	0.002	**	0.001	***	0.001	***	0.001	***
	3	<0.001	***	<0.001	***	<0.001	***	0.001	***
x = 0.01	0.375	0.05	*	0.002	**	0.001	***	0.02	*
	0.75	0.03	**	0.003	**	0.002	**	0.002	**
	1.5	0.02	**	0.001	***	0.001	***	0.01	**
	3	0.01	**	0.001	***	0.03	*	0.001	***
x = 0.02	0.375	0.005	**	0.002	**	0.003	**	0.002	**
	0.75	0.003	**	0.001	***	0.002	**	0.03	*
	1.5	0.02	*	0.001	***	0.001	***	0.001	***
	3	<0.001	***	0.001	***	<0.001	***	0.01	**

Table A1. Cont.

Sample	Nanoparticles Concentration (mg/mL)	Bacterial Isolates							
		Gram-Negative Bacteria				Gram-Positive Bacteria			
		<i>Escherichia coli</i>	S	<i>L. eclerciaade-carboxylata</i>	S	<i>Staphylococcus aureus</i>	S	<i>Enterococcus faecium</i>	S
		<i>p</i> -Values (vs. Water)							
x = 0.04	0.375	0.005	**	0.002	**	0.003	**	0.002	**
	0.75	0.003	**	0.001	***	0.002	**	0.002	**
	1.5	0.003	**	0.001	***	0.01	**	0.05	*
	3	<0.001	***	<0.001	***	0.001	***	0.001	***
	0.375	0.005	**	0.002	**	0.003	**	0.003	**
x = 0.08	0.75	0.02	*	<0.001	***	0.002	**	0.02	*
	1.5	0.002	**	0.001	***	<0.001	***	0.001	***
	3	<0.001	***	<0.001	***	0.01	**	0.01	**

S: significance, *p*-values were calculated such that: * *p* < 0.05, ** *p* < 0.01, *** *p* < 0.001.

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